

Non-Markovian quantum thermodynamics: second law and fluctuation theorems

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We bring together Keldysh theory and quantum thermodynamics, by showing that a real-time diagrammatic technique can provide a quantum equivalent of stochastic thermodynamics for non-Markovian quantum machines (heat engines, refrigerators, etc). Taking any interacting quantum system with arbitrary coupling to ideal reservoirs of electrons and bosons (phonons or photons), we identify symmetries between quantum trajectories and their time-reverses on the Keldysh contour. These lead to quantum fluctuations theorems the same as the well-known classical ones (Jarzynski and Crooks equalities, non-equilibrium partition identity, etc), but which hold whether the system's dynamics are Markovian or not. Hence, such systems obey the second law of thermodynamics on average, even if fluctuations may violate it. Our proof applies to systems with Kondo effects or other strong correlations, and to systems in superposition states or with time-dependent driving.

Introduction. The laws of thermodynamics were derived for macroscopic machines, where entropy-reducing fluctuations (such as all of a gas spontaneously drifting into one corner of its container) are so rare that they have been called “thermodynamic miracles” [1]. In contrast, in microscopic systems, these “miracles” become rather common, and it has been realized that they obey laws known as fluctuation theorems [2–5]. The most intuitive such theorem is that of Evans and Searles [6], which holds under steady-state conditions, it reads

$$P(-\Delta S, t) = P(\Delta S, t) \exp[-\Delta S] \quad (1)$$

where $P(\Delta S, t)$ is the probability that the entropy production is ΔS [7] during a time t . Hence, an entropy decrease is always less likely than the equivalent entropy increase. The second law of thermodynamics is satisfied on average, even if a fluctuation may violate it.

In classical systems, *stochastic thermodynamics* [8–13] is a unifying theory of fluctuation theorems; it gives

Eq. (1), and also the Jarzynski [14] and Crooks equalities [15, 16] in the relevant limits. Crucially, Ref. [8] used it to show that any classical system with Markovian dynamics obeys a non-equilibrium partition identity [17–19],

$$\langle \exp[-\Delta S] \rangle = 1, \quad (2)$$

whose direct consequence is the second law of thermodynamics, $\langle \Delta S \rangle \geq 0$. This classical theory applies directly to quantum systems with incoherent Markovian dynamics [9], and has been extended to other Markovian quantum systems using quantum trajectories [20].

Here we show that a Keldysh theory — the real-time diagrammatic technique [21–23] — provides an equivalent of stochastic thermodynamics for any quantum system coupled to reservoirs (Fig. 1), whether that system's dynamics are Markovian or not. We thereby show that such quantum systems respect the same fluctuation theorems as classical Markovian systems, and hence obey the second law of thermodynamics. Our proof relies on the observation that the contribution of a given double-trajectory, γ , on the Keldysh contour is related to the contribution of its time-reversed partner $\bar{\gamma}$ (Fig. 3a). This connection between quantum fluctuation theorems [3–5] and the Keldysh technique used in transport calculations for interacting systems [21–27], provides a powerful tool for understanding energy production and refrigeration at the nano-scale. The advantage over the elegant proofs in Ref. [3] is that we show the theorems apply to the exact and approximate diagrammatics that are used to model phenomena such as Coulomb blockade, resonant tunnelling, Kondo effect, etc [21–27]. At the level of the second law of thermodynamics, our proof goes beyond those for Markovian quantum systems [28], those for systems with mean-field interactions [29, 30], and Keldysh treatments for non-interacting systems (quadratic Hamiltonians) [31–33] or adiabatic driving [34].

Non-Markovian quantum heat-engines and refrigerators are of interest because Markovian approximations are usually only valid for weak-coupling to reservoirs (se-

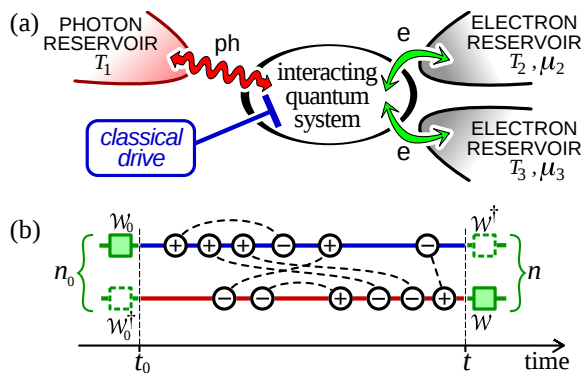


FIG. 1: (a) We consider a quantum system coupled to any number of electron reservoirs with chemical potentials and temperatures $\{\mu_\alpha, T_\alpha\}$, and photon or phonon reservoirs at temperatures $\{T_\alpha\}$. (b) A typical double Keldysh trajectory, γ , in which the horizontal lines represent the evolution of the system state, while the vertices indicate transitions within the system due to the coupling to one of the reservoirs.

quential tunnelling or similar approximations), which implies small heat and charge currents. Larger power outputs require stronger reservoir couplings, and hence non-Markovian effects. Keldysh methods can treat such situations for interacting systems far from equilibrium.

Hamiltonian. We consider an arbitrary interacting system Hamiltonian, \hat{H}_s , with any time-dependence. It can contain any hermitian combination of terms containing creation and annihilation operators for electronic states in the system, \hat{d}_i^\dagger and \hat{d}_i , so long as each term contains one annihilation operator for every creation operator. This system is coupled to multiple reservoirs of non-interacting fermions (electrons) via couplings $\hat{V}_{\text{el}}^{(\alpha)}$, or non-interacting bosons (photons or phonons) via couplings $\hat{V}_{\text{ph}}^{(\alpha)}$. These couplings may be of any strength and any time-dependence. The total Hamiltonian is

$$\hat{H} = \hat{H}_s + \sum_{\alpha \in \text{el}} [\hat{V}_{\text{el}}^{(\alpha)} + \hat{H}_{\text{el}}^{(\alpha)}] + \sum_{\alpha \in \text{ph}} [\hat{V}_{\text{ph}}^{(\alpha)} + \hat{H}_{\text{ph}}^{(\alpha)}]. \quad (3)$$

The sums are over electron (el) and photon/phonon (ph) reservoirs. For an electron reservoir, $\hat{H}_{\text{el}}^{(\alpha)} = \sum_k E_{\alpha k} \hat{c}_{\alpha k}^\dagger \hat{c}_{\alpha k}$, where $E_{\alpha k}$ is the energy for reservoir α 's state k , and $\hat{c}_{\alpha k}^\dagger$ and $\hat{c}_{\alpha k}$ are its creation and annihilation operators. The tunnel coupling is

$$\hat{V}_{\text{el};\alpha} = \sum_k (\hat{V}_{\alpha k}^+ \hat{c}_{\alpha k} + \hat{V}_{\alpha k}^- \hat{c}_{\alpha k}^\dagger) \quad (4)$$

where $\hat{V}_{\alpha k}^-$ and $\hat{V}_{\alpha k}^+$ contain only system operators, and may be time-dependent. The change in the system state when an electron is added from reservoir α 's state k is given by $\hat{V}_{\alpha k}^+$. The change when an electron is lost into reservoir α 's state k is given by $\hat{V}_{\alpha k}^-$, where $[\hat{V}_{\alpha k}^-]^\dagger = \hat{V}_{\alpha k}^+$. The simplest case has $\hat{V}_{\alpha k}^+ = \sum_i A_{ik}^{(\alpha)} \hat{d}_i^\dagger$. However, in general, the coupling can depend on the occupation of system states, then $\hat{V}_{\alpha k}^+$ may contain terms with many such operators, but with each term having one more creation than annihilation operator.

If reservoir α consists of bosons (photons or phonons), then one replaces the fermionic operators $\hat{c}_{\alpha k}^\dagger$ and $\hat{c}_{\alpha k}$ by bosonic operators. Then $\hat{V}_{\alpha k}^+$ and $\hat{V}_{\alpha k}^-$ give the change in the system state when a boson is absorbed from or emitted into reservoir α 's state k . In general $\hat{V}_{\alpha k}^+$ can have multiple terms, in which each term has one system creation operator for every annihilation operator.

We write all system operators as $N \times N$ matrices acting on the basis of N many-body system states. We go to an interaction representation (indicated by caligraphic symbols), where system operators evolve under a matrix $\mathcal{U}_s(\tau, t_0) = T \exp[-i \int_{t_0}^\tau H_s(t) dt]$, with T indicating time-ordering. Hence,

$$\mathcal{V}_{\alpha k}^\pm(\tau) = \mathcal{U}_s^\dagger(\tau; t_0) V_{\alpha k}^\pm(\tau) \mathcal{U}_s(\tau; t_0). \quad (5)$$

Reservoir operators evolve under $H_{\text{el/ph}}^{(\alpha)}$, so we have $\hat{c}_{\alpha k}^\dagger(\tau) = e^{iE_k(\tau-t_0)} \hat{c}_{\alpha k}^\dagger$ and $\hat{c}_{\alpha k}(\tau) = e^{-iE_k(\tau-t_0)} \hat{c}_{\alpha k}$.

The initial condition is a product state between the system and reservoirs at time t_0 . Each reservoir α is in its local equilibrium with temperature T_α and chemical potential μ_α ($\mu_\alpha = 0$ for reservoirs of photons or phonons). We treat H_s exactly, and take the standard “exact” treatment for finite couplings to infinite reservoirs; i.e. we take the coupling to each reservoir mode to zero as we take the number of reservoir modes to infinity. Then the coupling to each reservoir mode is treated at lowest-order (second-order). None the less, the system may interact with any number reservoir modes at one time (all orders of co-tunnelling events), and these interactions do not commute. The dynamics are thus highly non-Markovian, and capture strong correlation effects, such as the Kondo effect. The evolution can be represented as a double-trajectory such as Fig. 1b. Since we are in the interaction representation, the basis at all times is chosen such that the system state does not change unless there is an interaction with a reservoir. Transitions induced by the system-reservoir coupling occur as pairs with the same reservoir mode. Each pair can represent a real transition (D_{1+} in Fig. 2) or a virtual transition (D_{2+} or D_{3+} in Fig. 2).

Assumption of limited reservoir probes. The crucial assumption of this work is that we can probe arbitrary microscopic properties of the system states, but we are limited to probing only certain properties of the reservoir states. We refer to this as the assumption of *limited reservoir probes*. More precisely, we assume that probes of a reservoir are limited to measuring total energy and particle number in the reservoir at the beginning and end of an evolution. Thus, one *cannot* measure (or extract work from) the energy or phase of individual particles in the reservoir. We assume that we also know all macroscopic reservoir properties (T_α , μ_α , etc). Our proof will not apply if one probes another microscopic reservoir property, unless one can redefine that property as part of the system. The main consequence of this assumption is that measuring the reservoir state at the end of the evolution projects that reservoir into a state with definite energy and particle number, suppressing those terms in the density matrix associated with off-diagonal terms in the basis of reservoir modes. Even if the reservoir is not explicitly probed, weak interactions within the reservoir (or with external degrees of freedom) will anyway suppress such off-diagonal terms.

Entropy. The assumption of limited reservoir probes implies that entanglement between system and reservoir cannot be used to produce work. Then the correct definition of the total entropy production, ΔS , is the sum of that for the system (sys) and reservoirs (res),

$$\Delta S = \Delta S_{\text{sys}} + \sum_{\alpha} \Delta S_{\text{res}}^{(\alpha)} \quad (6)$$

with no term related to system-reservoir entanglement.

For any double-trajectory — such as that in Fig. 1b

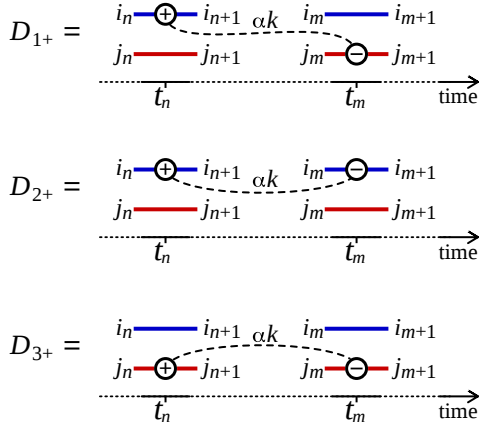


FIG. 2: The system's second-order interaction with reservoir α 's mode k . Vertices marked \oplus or \ominus corresponds to the matrices $\mathcal{V}_{\alpha k}^+$ or $\mathcal{V}_{\alpha k}^-$, respectively. The upper line is read from left to right, so the \oplus vertex in D_{1+} or D_{2+} indicates the matrix element $[\mathcal{V}_{\alpha k}^+]_{i_{n+1}i_n}$. The lower line is read from right to left, so the \oplus vertex in D_{3+} indicates the matrix element $[\mathcal{V}_{\alpha k}^+]_{j_n j_{n+1}}$. Interactions D_{a-} is given by D_{a+} (for $a = 1, 2, 3$) with $\oplus \leftrightarrow \ominus$.

— a dashed line is the system emitting a particle into (or absorbing a particle from) reservoir α 's mode k with energy E_k . Adding a particle to reservoir α does a work of μ_α . The remaining particle energy is heat ($E_k - \mu_\alpha$) in the reservoir, so reservoir α 's entropy change is [7],

$$\delta S_{\alpha k} = (E_k - \mu_\alpha)/T_\alpha. \quad (7)$$

If the system absorbs a particle from that state, the reservoir's entropy change is $-\delta S_{\alpha k}$. The sum of all such terms gives $\Delta S_{\text{res}}^{(\alpha)}$ for that trajectory.

For arbitrary system states, we can take ΔS_{sys} as the difference between the entropies of the system's initial and final states. To get this entropy for the system's initial density matrix (at time t_0), we write it as $\rho_{ml}^{\text{sys}}(t_0) = \sum_n [\mathcal{W}_0]_{mn} p_n(t_0) [\mathcal{W}_0^\dagger]_{nl}$, so $p_n(t_0)$ is the probability to find the system in state n of its diagonal basis. We associate a Boltzmann entropy weight of $-\ln[p_n(t_0)]$ to state n , so the average over all n gives the von Neumann entropy, $-\text{tr}[\rho_{\text{sys}}(t_0) \ln[\rho_{\text{sys}}(t_0)]]$. The final system state's entropy (at time t) is calculated in the same way by rotating to the diagonal-basis of the final system density matrix, given by $\rho_{ml}^{\text{sys}}(t) = \sum_n \mathcal{W}_{mn} p_n(t) [\mathcal{W}^\dagger]_{nl}$ for unitary \mathcal{W} , and assigning an entropy of $-\ln[p_n(t)]$ to the n th state in this diagonal basis.

Trajectories and their time-reverses. Consider an arbitrary double-trajectory γ on the Keldysh contour, in which the upper-line takes the system from a (many-body) state i_0 at time t_0 to state i at time t , while the lower line takes the state j_0 to the state j (see examples in Fig. 3a). Note that the matrix elements for transitions are time ordered on the upper line and reverse-time ordered on the lower line. Each transition takes the form

of one of the diagrams in Fig. 2, and these are multiplied together to get a trajectory's contribution, with extra minus signs for each crossing between dashed lines [23].

Contribution D_{1+} involves reservoir α 's entropy changing by $\delta S_{\alpha k}$ in Eq. (7), and it has a weight

$$D_{1+}^{\alpha k} = [\mathcal{V}_{\alpha k}^+(t_n)]_{i_{n+1}i_n} [\mathcal{V}_{\alpha k}^-(t_m)]_{j_m j_{m+1}} f_{\alpha k} e^{i\Phi_k^{mn}}, \quad (8)$$

for $t_n < t_m$ or $t_n > t_m$, where $\Phi_k^{mn} = E_k(t_m - t_n)$. The factor $f_{\alpha k} = (e^{\delta S_{\alpha k}} \pm 1)^{-1}$ with a $+$ sign for electron reservoirs (fermi factor) and a $-$ sign for photon or phonon reservoirs (bose factor). Other contributions often contain factors of $(1 - f_{\alpha k})$ for fermions or $(1 + f_{\alpha k})$ for bosons. These have the same form as each other via the fact that $(1 - f_{\alpha k}) = e^{\delta S_{\alpha k}} f_{\alpha k}$ for fermions, while $(1 + f_{\alpha k}) = e^{\delta S_{\alpha k}} f_{\alpha k}$ for bosons. Contribution D_{1-} involves an entropy change in reservoir α of $-\delta S_{\alpha k}$. Its weight is given by replacing $f_{\alpha k}$ by $e^{\delta S_{\alpha k}} f_{\alpha k}$ in Eq. (8) and taking its Hermitian conjugate (so $i\Phi_k^{mn} \rightarrow -i\Phi_k^{mn}$ and superscripts $+$ \leftrightarrow $-$). Contributions $D_{2\pm}^{\alpha k}$ and $D_{3\pm}^{\alpha k}$ involve no reservoir entropy change. Their weights are

$$D_{2+}^{\alpha k} = -[\mathcal{V}_{\alpha k}^-(t_m)]_{i_{m+1}i_m} [\mathcal{V}_{\alpha k}^+(t_n)]_{i_{n+1}i_n} f_{\alpha k} e^{i\Phi_k^{mn}},$$

$$D_{3-}^{\alpha k} = -[\mathcal{V}_{\alpha k}^-(t_n)]_{j_n j_{n+1}} [\mathcal{V}_{\alpha k}^+(t_m)]_{j_m j_{m+1}} f_{\alpha k} e^{-i\Phi_k^{mn}},$$

with $D_{2-}^{\alpha k}$ and $D_{3+}^{\alpha k}$ found by replacing $f_{\alpha k}$ by $e^{\delta S_{\alpha k}} f_{\alpha k}$, and taking a Hermitian conjugate.

Let us define a trajectory $\bar{\gamma}$ as the *time-reverse* of γ , for time-reversed states evolving under the time-reversed Hamiltonian. Whatever happens at time τ on the upper line in γ happens at a time $\bar{\tau} = t_0 + t - \tau$ on the lower line in $\bar{\gamma}$, and vice versa graphically this is the 180° shown in Fig. 3a. Defining \bar{i} is the time-reverse of state i [35, 36], the upper-line of $\bar{\gamma}$ goes from state \bar{j} at time t_0 to state \bar{j}_0 at time t , while its lower line goes from \bar{i} to \bar{i}_0 . The weights of γ and $\bar{\gamma}$ are given by products of the weights of the $D_{1\pm}$, $D_{2\pm}$ and $D_{3\pm}$ that form each of them. This leads to the *central observation* of this work (shown graphically in Fig. 3b),

$$\bar{P}(\bar{\gamma}) = P(\gamma) \exp[-\Delta S_{\text{res}}(\gamma)], \quad (9)$$

where $P(\gamma)$ is the weight of double-trajectory γ , $\bar{P}(\bar{\gamma})$ is the weight of $\bar{\gamma}$ under the time-reversed Hamiltonian. The entropy change in the reservoirs, $\Delta S_{\text{res}}(\gamma)$, is the sum over $\delta S_{\alpha k}$ for all the transitions that form γ .

To derive Eq. (9), we observe that if γ contains a factor of $D_{1\pm}^{\alpha k}(t_m, t_n)$, then $\bar{\gamma}$ contains a factor of $\bar{D}_{1\mp}^{\alpha k}(\bar{t}_n, \bar{t}_m)$. If γ contains $D_{2\pm}^{\alpha k}(t_m, t_n)$ then $\bar{\gamma}$ contains $\bar{D}_{3\mp}^{\alpha k}(\bar{t}_n, \bar{t}_m)$, and vice versa. Next, we chose the final states such that $\mathcal{U}_s^\dagger(t; t_0) = 1$, then one has $\mathcal{U}_s^\dagger(\tau; t_0) = \Theta \bar{\mathcal{U}}_s^\dagger(\bar{\tau}; t_0) \Theta^\dagger$, where Θ is the time-reverse operator [35, 36]. This means that $\bar{\mathcal{V}}(\bar{\tau}) = \Theta^\dagger \mathcal{V}(\tau) \Theta$, where $\bar{\mathcal{V}}(\bar{\tau})$ is the interaction representation coupling for time-reversed states under the time-reversed Hamiltonian. Then system operator matrix elements in $\bar{\gamma}$ are the same as in γ with $\bar{j}_n \leftrightarrow i_{m+1}$,

(a) Time-reversing trajectories : examples of the 180° rotation

$\gamma = \begin{array}{c} i_0 \text{---} i \\ j_0 \text{---} j \end{array}$	$\bar{\gamma} = \begin{array}{c} \bar{j}_0 \text{---} \bar{j} \\ \bar{i}_0 \text{---} \bar{i} \end{array}$
$i_0 \text{---} i = i_0$ $j_0 \text{---} j = j_0$	$\bar{j}_0 \text{---} \bar{j} = \bar{j}_0$ $\bar{i}_0 \text{---} \bar{i} = \bar{i}_0$
$i_0 \xrightarrow{t_1} i$ $j_0 \xrightarrow{t_2} j$	$\bar{j}_0 \xrightarrow{\bar{t}_2} \bar{j}$ $\bar{i}_0 \xrightarrow{\bar{t}_1} \bar{i}$
$i_0 \xrightarrow{t_1} i$ $j_0 \xrightarrow{t_2} j$	$\bar{j}_0 \xrightarrow{\bar{t}_2} \bar{j}$ $\bar{i}_0 \xrightarrow{\bar{t}_1} \bar{i}$
\vdots	\vdots
$i_0 \xrightarrow{t_1} i$ $j_0 \xrightarrow{t_2} j$	$\bar{j}_0 \xrightarrow{\bar{t}_2} \bar{j}$ $\bar{i}_0 \xrightarrow{\bar{t}_1} \bar{i}$

(b) $\begin{array}{c} i_0 \text{---} i \\ j_0 \text{---} j \end{array} \times e^{-\Delta S_{\text{res}}(\begin{array}{c} \text{ } \\ \text{ } \end{array})} = \begin{array}{c} \bar{j}_0 \text{---} \bar{j} \\ \bar{i}_0 \text{---} \bar{i} \end{array}$

FIG. 3: (a) A table giving some explicit examples of time-reversal via the rotation by 180° in the plane of the page. The times of the interactions are related by $\bar{t}_n = t + t_0 - t_n$. (b) A graphical representation of Eq. (9), where the shaded box is the weight of an arbitrary double-trajectory, $P(\gamma)$, and rotating that box by 180° gives its time-reverse, $P(\bar{\gamma})$.

$\bar{j}_{n+1} \leftrightarrow i_m$, $\bar{j}_m \leftrightarrow i_{n+1}$, and $\bar{j}_{m+1} \leftrightarrow i_n$. However, $D_{1+}^{\alpha k}$ contains an extra factor of $\exp[-\delta S_{\alpha k}]$ compared to $D_{1+}^{\alpha k}$. The difference between the weights of γ and $\bar{\gamma}$ is the product of these factors of $\exp[-\delta S_{\alpha k}]$, giving Eq. (9).

Fluctuation theorems. Now we consider a double-trajectory, γ_d , which goes from the n_0 th state in the diagonal basis of $\rho(t_0)$ to the n th state in the diagonal basis of $\rho_{ml}^{\text{sys}}(t)$ (see Fig. 1b). The subscript “d” is to indicate that it goes from diagonal basis to diagonal basis. The weight of γ_d equals that of γ above, multiplied by a factor of $[W_0]_{i_0 n_0} [W_0^\dagger]_{n_0 j_0}$ to transformation out of the diagonal basis at time t_0 , and a factor of $[W^\dagger]_{ni} W_{jn}$ to go to the diagonal basis at time t . We take the sum of the weights of each such path and its Hermitian-conjugate (graphically this is found by interchanging the trajectory’s upper and lower lines and taking $\oplus \leftrightarrow \ominus$). Each such contribution has a real weight, $P(\gamma_d)$. We see from Eq. (9) that the weight of the time-reversed path $\bar{\gamma}_d$ under the time-reversed Hamiltonian is $P(\bar{\gamma}_d) = P(\gamma_d) \exp[-\Delta S_{\text{res}}(\gamma_d)]$. This relation is the same as in Markovian stochastic thermodynamics [9, 11, 12], which is sufficient to extend the derivations of any fluctuation theorem to non-Markovian quantum systems. In particular, this means that any such system

obeys Eq. (2), and hence the second law of thermodynamics. The proof of this follows exactly as in Refs. [9, 11, 12], so here we only discuss specificities of our non-Markovian quantum theory.

To correctly assign an entropy to the system, one must take the initial and final density matrices in their respective diagonal bases, with trajectories going between these two bases. This requires knowing the final state density matrix, via a sum over all trajectories or another solution of the dynamics. This is much like in usual stochastic thermodynamics, where one needs the final state probability distribution to assign entropies to it.

In usual stochastic thermodynamics, the probability that a trajectory in state i has no transitions in the time window τ_n to τ_{n+1} is $\exp[-\int_{\tau_n}^{\tau_{n+1}} d\tau \Gamma_i(\tau)]$, where $\Gamma_i(\tau)$ is the sum of all transition rates out of state i at time τ [9, 11, 12]. To compare this with our quantum theory (which is perturbative in the reservoir couplings), such exponential terms should be expanded in powers of Γ . This generates a version of stochastic thermodynamics in which trajectories can have positive or negative weights. Our quantum theory has trajectories with positive and negative weights for the same reason.

There is a non-zero weight for double-trajectories going from n_0 in the initial state’s diagonal basis to n and n' on the upper and lower lines in the final state’s diagonal basis, with $n' \neq n$. However, their sum is zero, since W diagonalizes the final density matrix. This means that they only inform us about system-reservoir correlations which do not affect $\langle \Delta S \rangle$. As we follow the logic in usual stochastic thermodynamics, and get final state entropies from the sum over all trajectories, such trajectories also play no role in the distribution of ΔS .

Approximate theories. Any approximation which contains a trajectory $\bar{\gamma}$ for every trajectory γ will obey Eq. (9) and so obey all the usual fluctuation theorems. This applies for approximations that include all irreducible diagrams up to a given order in system-reservoir coupling. Thus the Markovian theory given by the sequential-tunnelling or golden-rule approximation, will respect the fluctuation theorems (and hence the second law) even if initial and final states are coherent superpositions in the system’s energy eigenbasis. Systematically including higher-order (co-tunnelling) events, will also give theories which respect fluctuation theorems.

Conclusions. We have proposed an equivalent of stochastic thermodynamics using a real-time Keldysh theory for arbitrary quantum systems coupled to ideal reservoirs, which can be performed either exactly or with certain well-known approximations. Whether such systems are Markovian or not, we have shown that they obey the second law of thermodynamics and the same fluctuation relations as classical Markovian systems. This provides a powerful tool to analyse energy-harvesting and refrigeration in out-of-equilibrium nanoscale systems.

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- [1] see chapter 6 of Gérard Battail, *Information and Life*, (Springer, 2014).
 - [2] E.M. Sevcik, R. Prabhakar, S.R. Williams, and D.J. Searles, Fluctuation Theorems, *Annu. Rev. Phys. Chem.* **59**, 603 (2008).
 - [3] M. Campisi, P. Hänggi, and P. Talkner, Quantum Fluctuation Relations: Foundations and Applications, *Rev. Mod. Phys.* **83**, 771 (2011).
 - [4] S. Vinjanampathy, and J. Anders, Quantum Thermodynamics, *Contemporary Physics*, **57**, 1 (2016).
 - [5] J. Millen, and A. Xuereb, Perspective on quantum thermodynamics, *New J. Phys.* **18**, 011002 (2016).
 - [6] D.J. Evans, and D.J. Searles, Equilibrium microstates which generate second law violating steady states, *Phys. Rev. E* **50**, 1645 (1994).
 - [7] We take entropy in units of k_B , temperature in units of energy, and time in units of $1/(\text{energy})$; so $\hbar = k_B = 1$.
 - [8] U. Seifert, Entropy production along a stochastic trajectory and an integral fluctuation theorem, *Phys. Rev. Lett.* **95**, 040602 (2005).
 - [9] T. Schmiedl and U. Seifert, Stochastic thermodynamics of chemical reaction networks, *J. Chem. Phys.* **126**, 044101 (2007).
 - [10] U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, *Rep. Prog. Phys.* **75**, 126001 (2012).
 - [11] C. Van den Broeck and M. Esposito, Ensemble and Trajectory Thermodynamics: A Brief Introduction, *Physica A* **418**, 6 (2015).
 - [12] Section 8.10 in G. Benenti, G. Casati, K. Saito, and R.S. Whitney, Fundamental aspects of steady-state conversion of heat to work at the nanoscale, *Eprint - arXiv:1608.05595*.
 - [13] U. Seifert, First and Second Law of Thermodynamics at Strong Coupling, *Phys. Rev. Lett.* **116**, 020601 (2016).
 - [14] C. Jarzynski, Nonequilibrium equality for free energy differences, *Phys. Rev. Lett.* **78**, 2690 (1997). C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach, *Phys. Rev. E*, **56**, 5018 (1997).
 - [15] G. Crooks, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, *Phys. Rev. E* **60**, 2721 (1999).
 - [16] H. Tasaki, Jarzynski relations for quantum systems and some applications, *Eprint: condmat/0009244*.
 - [17] T. Yamada and K. Kawasaki, Nonlinear Effects in the Shear Viscosity of Critical Mixtures, *Prog. Theor. Phys.* **38** 1031 (1967).
 - [18] G.P. Morriss and D.J. Evans, Isothermal response theory, *Mol. Phys.* **54**, 629 (1985).
 - [19] D. M. Carberry, S. R. Williams, G. M. Wang, E. M. Sevcik and D. J. Evans, The Kawasaki identity and the fluctuation theorem, *J. Chem. Phys.* **121**, 8179 (2004).
 - [20] C. Elouard, D. Herrera-Mart, M. Clusel, and A. Auffèves, The role of quantum measurement in stochastic thermodynamics, *Eprint - arXiv:1607.02404*.
 - [21] J. König, J. Schmid, H. Schoeller, and G. Schön, Resonant tunneling through ultrasmall quantum dots: Zero-bias anomalies, magnetic-field dependence, and boson-assisted transport, *Phys. Rev. B* **54**, 16820 (1996).
 - [22] J. König, H. Schoeller, and G. Schön, Cotunneling at Resonance for the Single-Electron Transistor, *Phys. Rev. Lett.* **78**, 4482 (1997).
 - [23] H. Schoeller, Transport theory of interacting quantum dots, in *Mesoscopic Electron Transport*, L.L. Sohn, L.P. Kouwenhoven, G. Schön (Eds.) NATO-ASI Series E : Applied Sciences, **345** (Springer, 1997), online at <http://digbib.ubka.uni-karlsruhe.de/volltexte/documents/2135>.
 - [24] H. Schoeller, A perturbative nonequilibrium renormalization group method for dissipative quantum mechanics Real-time RG in frequency space, *Eur. Phys. Journ. Special Topics* **168**, 179 (2009).
 - [25] R.B. Saptsov and M.R. Wegewijs, Time-dependent quantum transport: Causal superfermions, exact fermion-parity protected decay modes, and Pauli exclusion principle for mixed quantum states, *Phys. Rev. B* **90**, 045407 (2014).
 - [26] B. Sothmann, Electronic waiting-time distribution of a quantum-dot spin valve, *Phys. Rev. B* **90**, 155315 (2014).
 - [27] J. Schulenburg, R.B. Saptsov, F. Haupt, J. Splettstoesser, and M.R. Wegewijs, Fermion-parity duality and energy relaxation in interacting open systems, *Phys. Rev. B* **93**, 081411 (2016).
 - [28] for a review see R. Kosloff, Quantum Thermodynamics, *Entropy* **15**, 2100 (2013).
 - [29] G. Nenciu, Independent electron model for open quantum systems: Landauer-Büttiker formula and strict positivity of the entropy production, *J. Math. Phys.* **48**, 033302 (2007).
 - [30] R.S. Whitney, Thermodynamic and quantum bounds on nonlinear DC thermoelectric transport, *Phys. Rev. B* **87**, 115404 (2013).
 - [31] M.F. Ludovico, J.S. Lim, M. Moskalets, L. Arrachea, and D. Sánchez, Dynamical energy transfer in ac driven quantum systems, *Phys. Rev. B* **89**, 161306(R) (2014).
 - [32] M. Esposito, M.A. Ochoa, and M. Galperin, Quantum Thermodynamics: A Nonequilibrium Green’s Functions Approach, *Phys. Rev. Lett.* **114**, 080602 (2015).
 - [33] A. Bruch, M. Thomas, S.V. Kusminskiy, F. von Oppen, and A. Nitzan, Quantum thermodynamics of the driven resonant level model, *Phys. Rev. B* **93**, 115318 (2016).
 - [34] M.F. Ludovico, M. Moskalets, D. Sánchez, and L. Arrachea, Dynamics of energy transport and entropy production in ac-driven quantum electron systems, *Phys. Rev. B* **94**, 035436 (2016).
 - [35] see e.g. chapt. XV of A. Messiah, *Quantum Mechanics* (North Holland, Amsterdam, 1962)
 - [36] see e.g. section IV A of Ref. [3].